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Negative electron affinity mechanism for diamond surfaces

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The energy distribution of the secondary electrons for chemical vacuum deposited diamond films with negative electron affinity (NEA) was investigated. It was found that while for completely hydrogenated diamond surfaces the negative electron affinity peak in the energy spectrum of the secondary electrons is present for any energy of the primary electrons, for partially hydrogenated diamond surfaces there is a critical energy above which the peak is present in the spectrum. This critical energy increases sharply when hydrogen coverage of the diamond surface diminishes. This effect was explained by the change of the NEA from the true type for the completely hydrogenated surface to the effective type for the partially hydrogenated surfaces. [S0003-6951(98)03120-9]

One of the remarkable properties of diamond is negative electron affinity (NEA) of its surfaces covered by hydrogen.¹ A surface has the property of NEA when the vacuum energy level lies below the conduction band minimum. It allows electrons to escape easily into the vacuum.² Semiconductors with NEA are widely used as photocathode and cold-cathode emitters.

NEA in diamond is often studied using ultraviolet photoelectron³⁻⁵ or secondary electron⁶⁻⁸ spectroscopy. Hot electrons, excited with photons or high energy primary electrons into the conduction band, cool in the process of energy relaxation, and accumulate in the conduction band minimum. At an NEA surface these electrons can be emitted into the vacuum without any energy barrier and appear in the photoemission or the secondary electron spectra as a sharp peak at low electron energies.

There are two ways to model the NEA phenomenon (Fig. 1). It can be done in terms of either true or effective negative electron affinity. The effective NEA model can be described as a combination of positive electron affinity and depletion band bending at the surface of the semiconductor. This band bending can result in the vacuum energy level occurring at an energy below the minimum of the conduction band.² The magnitude of the effective NEA is determined as $\chi_{\text{eff}} = \phi_{\text{BB}} - \chi$, where ϕ_{BB} is band bending and χ is positive electron affinity [Fig. 1(a)]. In the case of true NEA, χ becomes negative due to the existence of a dipole layer on the semiconductor surface and the NEA effect can be observed even for flatbands near the surface. Existence of the depletion band bending in this case increases the NEA effect, so $\chi_{\text{true}} = \phi_{\text{BB}} + \chi$ [Fig. 1(b)].

It has been argued that the true NEA model can be applied to the surfaces of natural crystal diamond even in the case of the existence of band bending near its surface.⁵ There are also speculations that some properties of the energy distribution of the secondary electrons from the surface of highly doped chemical vapor deposition (CVD) diamond

films can be described more accurately in terms of the effective, rather than the true, NEA.⁶

In this work we investigate the energy distribution of the secondary electrons from CVD diamond polycrystalline films and demonstrate that the type of NEA depends on the extent of hydrogen coverage of the diamond surface.

The samples were made by depositing 10–20 μm continuous films on Mo substrates by microwave-plasma CVD. During the deposition process, the films were heavily doped with boron up to a concentration of $N_A \approx (10^{18} - 10^{19}) \text{ cm}^{-3}$ which was estimated from the film conductivity measurements.

The samples were mounted on a heater which was positioned at the center of an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} Torr. To clean the surfaces before the measurements, the films were annealed at 500 °C for 30 min. After that, the samples underwent multiple cycles (5–10) of rehydrogenation. Each cycle included sample annealing at temperatures higher than 950 °C (to remove hydrogen from the surfaces) and subsequent room-temperature exposure of the diamond to atomic hydrogen.⁹ Atomic hydrogen was produced from the molecular hydrogen background by a hot tungsten filament heated to temperatures about 1900 °C. The surfaces, treated in this way, demonstrated NEA which was uniform over the entire surface and was also reversible. The surfaces had a coefficient of the secondary electron

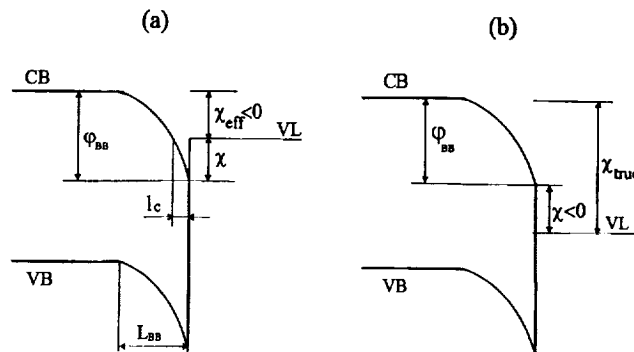


FIG. 1. Near the surface band diagram of a semiconductor for (a) effective NEA and (b) true NEA models. CB, VB, and VL are conduction band, valence band, and vacuum level, correspondingly.

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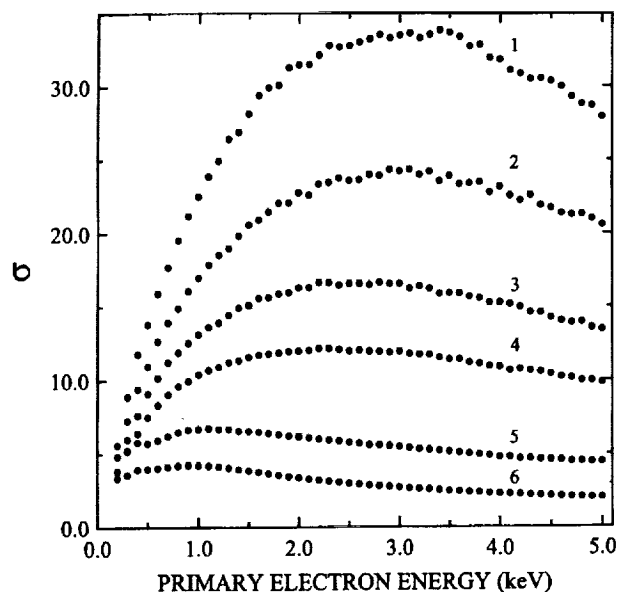


FIG. 2. $\sigma(E_p)$ after sample heating at various temperatures ($^{\circ}\text{C}$): (1) 500, (2) 600, (3) 700, (4) 750, (5) 850, and (6) 975.

emission (SEE) of up to 50 at the primary electron energy $E_p = 3$ keV. Auger spectra of the treated surfaces did not show any elements other than carbon.

Secondary electron spectra were measured by a single-pass (Perkin-Elmer) cylindrical mirror analyzer (CMA) with an energy resolution of 0.6% and a collection angle of $42 \pm 6^{\circ}$. During the measurements all the samples were biased at voltages $V_t = -(0.5-5)\text{V}$ to compensate for the work function difference between the target and the analyzer and to make the measurements of the very low energy region of the spectrum reliable. In this range of the applied bias, the measured electron spectra shifted linearly with the voltage. The energy of secondary electrons in these spectra was measured with respect to the Fermi level of the sample. The position of the Fermi level was determined from the location of the " σ peak" in the secondary electron spectrum of a graphite sample (Aquadag).¹⁰

The extent of surface hydrogen coverage was changed by heating the sample at increasingly higher temperatures in the range of 600–975 $^{\circ}\text{C}$ in 10 min increments. After each heating step the coefficient of SEE, σ , was measured as a function of E_p using the pulse method which was described in detail in Ref. 11. The maximum value of $\sigma(E_p)$ was considered a measure of the surface hydrogen coverage.

Figure 2 shows the $\sigma(E_p)$ curves measured after heating the sample at various temperatures. It can be seen that σ decreased monotonically when the temperature was increased from 600 to 950 $^{\circ}\text{C}$. The effect is evidently due to gradual hydrogen desorption from the sample surface.^{12–14} In our experiments we were not able to observe any increase of σ after the sample was heated at temperatures above 500 $^{\circ}\text{C}$ as was described in Ref. 8.

Figure 3 demonstrates the behavior of the low energy part of the secondary electron energy distribution versus the energy of primary electrons at various hydrogen coverages of the CVD diamond surface. The data in Fig. 3(a) were obtained immediately after the surface was saturated with hydrogen in the course of rehydrogenation and the sample had

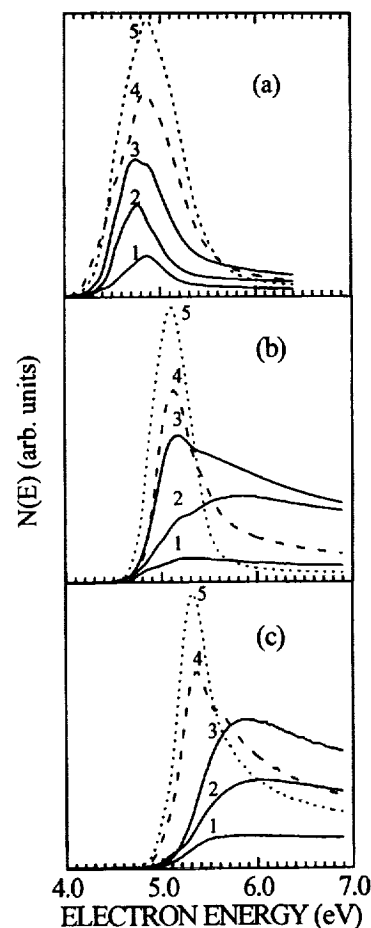


FIG. 3. Spectra of secondary electron energy distribution $N(E)$ at various E_p (keV) for surfaces with different σ : (a) $\sigma = 35$; (1) 0.01, (2) 0.20, (3) 1.0, (4) 2.0, (5) 3.5; (b) $\sigma = 8$; (1) 0.01, (2) 0.5, (3) 1.0, (4) 2.0, (5) 4.0; (c) $\sigma = 4$; (1) 0.01, (2) 0.20, (3) 1.0, (4) 3.0, (5) 4.0.

a maximum value of $\sigma = 35$. In this case the low energy peak, which is characteristic for NEA surfaces, was observed to appear even at the lowest energy of the primary electrons (10 eV) reported here.¹⁵ A fine structure which can be seen in the peak was earlier shown⁷ to reflect the energy structure of the diamond conduction band.

A reduction of σ and hydrogen coverage, correspondingly, resulted in emergence of some critical value of the primary electron energy (E_p^c), above which the NEA peak was observed in the energy spectrum of the secondary electrons. As it follows from Figs. 3(b) and 3(c), the lower the value of σ , the higher the magnitude of E_p^c .

Figure 4 displays the dependence of E_p^c on σ . E_p^c was determined as the value of E_p at which the NEA peak appears above the background. In the range of σ from 35 to 12, the NEA peak was observed at all primary energies used in our experiments, and the minimum value of $E_p = 10$ eV, reported in this letter, is shown in the plot as E_p^c for these coverages. At lower hydrogen coverages ($\sigma < 12$) E_p^c grows sharply and reaches 3 keV at $\sigma = 4$.¹⁶

These experimental data are consistent with the notion that the type of NEA changes in the process of the hydrogen desorption from the diamond surface. It was suggested earlier⁵ that after rehydrogenation diamond has downward band bending at the surface and has a true type of NEA [Fig. 1(b)]. This model agrees with our observation of the NEA

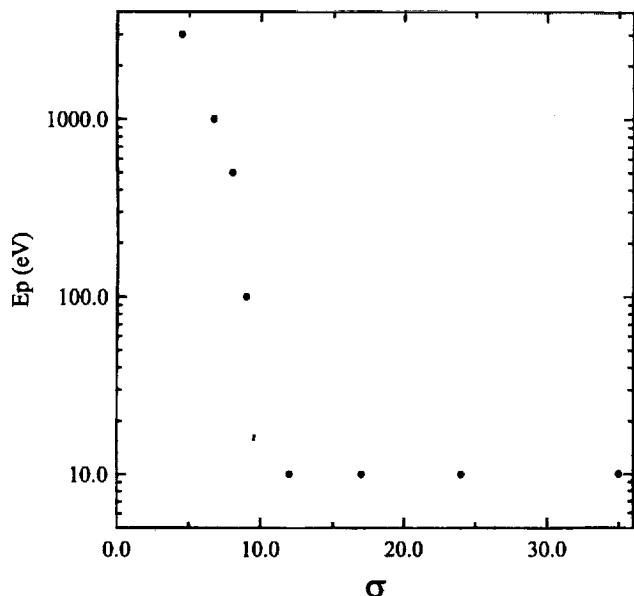


FIG. 4. Dependence of the critical energy E_p^c vs σ .

peak at very low primary electron energies on the completely rehydrogenated surface. Indeed, at $E_p \leq 100$ eV the penetration depth of the primary electrons, l_p , is only several interatomic layers¹⁷ and, therefore, the existence of even a very low potential surface barrier would prevent the low energy secondary electrons from escaping the solid. The critical height of the barrier can be estimated as $\chi_c \approx \phi_{BB} l_p / L_{BB}$, where ϕ_{BB} is the band bending and L_{BB} is the length of the depletion layer (Fig. 1). At $\chi > \chi_c$, the electrons accumulated at the bottom of the conduction band within l_p of the surface and cannot escape the crystal. For our highly doped CVD films ($N_A \approx 10^{18} - 10^{19} \text{ cm}^{-3}$) the Fermi-level position can be estimated at (0.3–0.4) eV above the top of the valence band in the bulk. In the case of true NEA, the onset of the low energy peak corresponds to the bottom of the conduction band at the surface and, as it follows from Fig. 3, is equal to 4.3 eV. Then, using the value of 5.5 eV for the diamond band gap, we obtain $\phi_{BB} \approx 1$ eV, and $L_{BB} = (\phi_{BB} \kappa / 2\pi e N_A)^{1/2} \approx (100 - 300) \text{ \AA}$ (here κ is the diamond dielectric constant and e is the electron charge). At $l_p \approx 10 \text{ \AA}$, the potential barrier $\chi_c \approx (0.03 - 0.1) \text{ eV}$. Therefore, from the data presented in Fig. 3, we can conclude that for the diamond surface saturated with hydrogen χ is at least less than kT at room temperature and most probably negative.

The fact that there is a critical potential E_p^c for a surface with partially desorbed hydrogen indicates that the work function becomes positive and NEA transforms to the effective type. In the latter case, the NEA peak can be observed only when the penetration depth of the primary electrons is larger than a critical depth $l_c \approx \chi_c L_{BB} / \phi_{BB}$ (Fig. 1). On the other hand, if $l_p \leq l_c$ the low energy secondary electrons are captured by the surface potential well and cannot escape the surface. It is well known¹⁶ that l_p increases with the increase of the primary electron energy and, as it is clear from Fig. 1, the increase of χ_c should result in a shift of E_p^c to higher values. In the model of effective NEA, the onset of the NEA peak corresponds to the vacuum level and also has to move to higher energies. This agrees with the experimental data displayed in Fig. 3. It can be seen that the NEA peak onset

shifts by approximately 0.6 eV to higher energy when σ decreases from 35 to 4. The shift of the onset can result from both the increase of χ and the change of the band bending. If we assume that all the shift is due to the change in χ , and for the surface saturated with hydrogen $\chi \leq 0$, we can estimate for the surface with $\sigma = 4$ the upper limit for $l_c \approx 0.6 L_{BB} \approx 100 \text{ \AA}$, which is close to value of l_p for electrons with energy equal to 3 keV.¹⁶

In conclusion, we have shown that the existence of an NEA peak in the energy spectrum of the secondary electrons for the partially hydrogenated diamond surface depends on the energy of the primary electrons. There is a critical primary energy value (E_p^c) at which the NEA peak appears in the spectrum. E_p^c grows sharply at declining hydrogen coverage of the diamond surface. The effect has been explained by the change of the NEA from the true type for fully hydrogenated surface to the effective type for the partially hydrogenated surface.

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¹⁵ For such low energies of the primary electrons impact excitation of electrons from the valence band is not effective because in order to satisfy the laws of energy and momentum conservation E_p should be higher than $2E_g$ (precise threshold value of E_p depends on a semiconductor band structure). The secondary electrons in this case are mostly the primaries which escaped to vacuum after energy relaxation in the process of optical phonon scattering inside the crystal.

¹⁶ We observed the similar effects on (100) and (111) faces of the 2b natural diamond.

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